

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Fillers for Rubber or Other Vulcanisable Substances

- We, COMPAGNIE INDUSTRIELLE DE CRÉDIT, a Corporation organised under the laws of the French Republic, residing at 51, rue d'Anjou, Paris, France, do hereby
- 5 declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—
- 10 The present invention relates to such fillers as are employed in the composition of rubber mixtures and relates more particularly to carbon blacks obtained
- 15 through partial combustion of natural gases from oil fields—(the so-called active or reinforcing blacks). It is known that one of the main uses of these blacks is to act as filler in rubber mixtures. Their use enables mixtures to be obtained suitable
- 20 for yielding vulcanised products having very high mechanical properties and particularly a very good resistance to wear. These properties are extensively used in the tyre industry. Besides the
- 25 aforesaid advantages, the use of these carbon blacks has disadvantages one of the foremost being the variation of the vulcanization time period. Thus generally, the use of oil gas blacks, which
- 30 impart the highest resistance to wear to the mixtures, is often accompanied by a very noticeable extension of the time of vulcanization at a given temperature compared to that obtainable with other fillers
- 35 such as chalk or zinc oxide. This effect is particularly marked when the mixture is accelerated by means of accelerators having an acid character, such as mercaptobenzothiazol.
- 40 On the other hand, such accelerators are those which at present possess the most useful properties for tyre mixtures. The result thereof is that the use of such carbon blacks, particularly for tyre mix-
- 45 tures, is associated with a substantial extension of the time of vulcanization, and therefore involves a smaller output from the moulding appliances, a greater fuel consumption and a higher installation cost. Such drawbacks are
- 50 not restricted to these types of blacks, but they appear also to different degrees with the use of most fillers such as certain carbon blacks proper, china-clays and colloidal silicas, colloidal alumina, and
- 55 some kinds of bentonites.
- A feature of this invention is to submit the fillers showing such a characteristic, previous to their use in the mixtures, to a treatment whereby the drawback of the
- 60 extension of the time of vulcanization is suppressed, thus obtaining with these fillers as quick vulcanisation as can be obtained with non-retarding fillers.
- This treatment consists in causing the
- 65 filler to adsorb primary or secondary amines so that the latter are present in the mixtures during vulcanisation. It has been generally noticed that rubber fillers increasingly delay vulcanisation as their acid character increases in conjunction with a high degree of adsorption. By treating such a filler as stated
- 70 hereinabove by adsorption of primary or secondary amines, the acid character can be reduced to a very large extent, as well as the further capacity of adsorption. The result thereof will be that the filler
- 75 thus treated will have less tendency to delay the vulcanization than before such treatment. It is possible, through a suitable choice of the nature and quantity of the adsorbed substance to obtain fillers
- 80 which will not delay vulcanization or which may even have an accelerating effect.
- The mechanical properties of the mixtures will not be reduced and they may even be noticeably increased.
- 85 The substances suitable for practical use include, by way of example, and without this list being considered as

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limitative, monobutylamine, dibutylamine, piperidine, aniline, ortho-toluidine, paratoluidine and alphanaphthylamine. The choice of these substances

5 will be determined by conditions of use and by economical considerations.

The adsorption of the selected substance may be effected in a variety of ways.

10 Adsorption may be effected in the liquid phase, by dissolving or emulsifying the base in a suitable liquid, and by suspending the fillers to be treated in this solution or emulsion. When the desired quantity of base has been adsorbed by the 15 filler, which may be ascertained by determining said base in the supernatant liquid, the filler is filtered and dried. The base may further be dissolved in a volatile solvent, the filler suspended there- 20 in and the solvent, evaporated, whereafter the solvent may be recovered through ordinary processes.

25 Adsorption in the gaseous phase may be also used by passing over the filler a gaseous stream containing a proportion the vapour of the amine selected.

30 The quantity of base necessary to balance exactly the vulcanization delay caused by the filler is dependent on the nature of the latter and on the nature and amount of accelerator utilized in the mixture. As it would be tiresome to pre- 35 pare several differently treated batches of the same filler, it will be generally

preferable to treat a single batch thereof 35 with an excess amount of base and use this treated filler in admixture with the non-treated filler in proportions easily determined by experience.

40 Four examples of the process according to the invention are illustrated herein-after.

EXAMPLE 1.

An oil gas black of the "channel black" type commonly used in mixtures 45 for pneumatic tyres is treated as follows. A 2.5 grams per litre dibutylamine aqueous solution is prepared. To five litres of this solution, 1 kilogram of black is added. The mixture is vigorously 50 agitated, the suspension being left to stand for one hour. At the end of this period the supernatant liquid is decanted and then the black sludge is filtered. After draining, the sludge is submitted 55 to the action of a press to eject the greater part of the interposed liquid, and then dried for twelve hours in a hot-air stove at 70° C. After this time the mixture is left to cool off, then pulverized and sifted. 60 The black thus prepared is tested in two rubber mixture formulæ corresponding to the composition given below, and only differing as regards the quantity of accelerator used. At the same time a 65 black of the same kind is tested which has not been submitted to the above treatment.

	Smoked sheets	100	100	100	100
70	Zinc oxide	5	5	5	5
	Stearic acid	4	4	4	4
	Sulphur	2.5	2.5	2.5	2.5
	Pine tar	5	5	5	5
	Mercaptobenzothiazol	0.75	7.25	0.75	1.25
75	Non-treated black	50	50	50	50
	Treated black	—	—	—	—
	Test No.	A	B	C	D

80 With the mixtures thus obtained, methodical tests are made for vulcanisation as well as for measuring mechanical properties of the product, by apply-

ing the customary methods employed in the rubber industry. The following results are obtained:

85	Composition	A	B	C	D
	Duration of vulcanization at 143° C. which gives the best stress resisting properties	60 min.	50 min.	30 min.	20 min.
90	Maximum breaking capacity Kg/cm ²	260Kg/cm ²	290Kg/cm ²	310Kg/cm ²	335Kg/cm ²
	Breaking elongation %	550	525	525	610
	Shore hardness	58	65	65	68
95	Wear index in cm ³ /KWh (Pont process) i.e. method of Du Pont De Nemours)	250	230	220	205

It is evident, from these results, that the duration of the vulcanisation which gives the best physical properties was

greatly reduced and that the physical 10 properties were clearly improved during the treatment. On the other hand, if the

properties of mixture B are considered as sufficient, it will be seen that they can be attained or even exceeded with mixture C by using treated black and a reduced amount of accelerator, which is an appreciable economy.

EXAMPLE 2.

21 gr. of dibutylamine are dissolved in 3 litres of ethyl alcohol. To this solution 1 Kg. of the same black as in the preceding example is added. The mixture is agitated so as to obtain an homogeneous sludge. This sludge is laid in thin layers on metal plates and dried in a stove at 70° C. for 4 hours. After this time the brittle mass is pulverised. The

Mixture
35 Duration of vulcanization at 143° which provides the best stress resisting properties
Breaking capacity in Kg/cm²
Breaking elongation %
40 Wear index in cm³/KWh (Pont process)

It will be readily understood from the preceding results that it is possible, though using a smaller amount of accelerator, to obtain simultaneously better physical properties and a substantially reduced vulcanization period.

EXAMPLE 3.

An aqueous dibutylamine solution of 2.5 grm. per litre is prepared. Into 5 litres of this solution 1 Kg. of very fine carbon black of rubber quality is poured. The mixture is vigorously agitated and left to stand for one hour. After this period, the floating liquid is decanted and will be available for a further operation after its dibutylamine content has been restored to its original value. The black sludge is filtered, dried for 12 hours at 70° C. and then pulverised. With the carbon black

Composition
Duration of vulcanization at 143° C. providing the best stress resisting properties
85 Maximum breaking resistance Kg/cm²
Maximum breaking elongation %
Shore hardness
Wear index in cm³/KWh (Pont process)

90 From the preceding results, the improvement in physical properties resulting from the treatment are obvious.

EXAMPLE 4.

An aqueous solution containing 2.5 gr. per litre of dibutylamine is prepared. Into 5 litres of this solution, 1 Kg. of

black thus obtained is tested by comparison with a non-treated black in the following mixtures:

Smoked sheets	100	100	20
Zinc oxide	5	5	
Stearic acid	6	6	
Sulphur	2.5	2.5	
Pine tar	8	8	
Tetraethylthiuram disulphide	0.5	0.3	25
Non-treated black	100	—	
Treated black	—	100	
Mixture	E	F	

With the mixture hereinabove, the same tests are made as for the preceding example, and the following results are obtained:

E	F
8 min.	8 min.
180Kg/cm ²	240Kg/cm ²
350	320
500	390

thus treated and a black in its pre-treatment condition two mixtures are prepared corresponding to the compositions hereinafter:

Smoked sheets	100	100	65
Zinc oxide	10	10	
Stearic acid	3	3	
Sulphur	2.5	2.5	
Pine tar	5	5	70
Tetramethylthiuram monosulphide	0.25	0.25	
Benzothiazyl disulphide	0.25	0.25	
Non-treated carbon black	140	—	75
Treated carbon black	—	140	
Mixture	G	H	

After the same tests as for the two preceding examples have been made, the following results are obtained:

G	H
15 min.	10 min
60Kg/cm ²	112Kg/cm ²
280	350
72	84
1570	1220

china clay passing entirely in a 305 mesh/in. sieve, is poured, the mixture being then vigorously agitated. After 5 hours of contact, the liquid is filtered through a filter of very fine-texture paper. The liquid filtered off may be used for further operations, after its base content has been restored. The filtered china

clay sludge is dried at 70° and pulverized. The china clay obtained is tested by comparison with non-treated china clay, in the following mixtures:—

5	White crepe rubber	100	100
	Zinc oxide	10	10
	Stearic acid	2	2
	Sulphur	2.5	2.5

Tetramethylthiuram monosulphide	0.25	0.25	10
Non-treated china clay	200	—	
Treated china clay	—	200	
Mixture	I	J	

These mixtures were tested according to the preceding examples and gave the following results:

	Mixture	I	J
20	Duration of vulcanization at 143° C. providing the best stress resisting properties	10 min	8 min.
	Maximum breaking resistance in Kg/cm ²	68Kg/cm ²	105Kg/cm ²
	Breaking elongation %	290	320
	Shore hardness	65	77
25	Wear index in cm ² /KWh (Pont method)	2250	1650

The improvement resulting from the treatment according to the present invention is clearly controllable from the above results.

30 In the preceding specification as well as in the following claims, reference is made to the word "rubber" to designate synthetic, natural or reclaimed caoutchouc or latex individually in
35 mixture.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we
40 claim is:—

1. A method of preparing a vulcanised rubber mixture containing a filler that normally increases the time required for vulcanisation, wherein a primary or
45 secondary amine is fixed on the filler by adsorption so as to be present in the mixture during vulcanisation.

2. A method as claimed in claim 1 wherein an accelerator is also present in
50 the mixture during vulcanisation.

3. A method of preparing a vulcanised

rubber mixture in which there is present during the vulcanisation an accelerator having an acid character and a carbon black filler having a primary or secondary amine fixed thereon by adsorption. 55

4. A vulcanisable rubber mixture comprising an accelerator, a filler that normally increases the time of vulcanisation, and a primary or secondary amine
60 fixed on said filler by adsorption.

5. The vulcanisable rubber mixtures substantially as hereinbefore described.

6. The methods of preparing vulcanisable rubber mixtures containing fillers
65 that normally increase the time of vulcanisation, substantially as hereinbefore described.

7. Vulcanised rubber which contains a filler that normally increases the time
70 required for vulcanisation, when prepared by any of the methods claimed in claim 1 to 3.

Dated this 18th day of April, 1947.

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